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(54) Separator for solid polymer type fuel cell and process for producing the same

(57) A separator for solid polymer-type fuel cell is produced by molding the resin composition which comprises an electroconductive agent and a radical-polymerizable thermosetting resin system by a resin molding method. The electroconductive agent comprises a carbon powder. The radical-polymerizable thermosetting resin system may comprise a radical-polymerizable resin (especially, a vinyl ester-series resin) and a radical-polymerizable diluent. It is preferred that the double bond equivalent of the radical-polymerizable resin may about 200 to 1,000 and that the hardened radical-polymerizable thermosetting resin system has a glass transition temperature of 120 oC or more. The weight ratio of the electroconductive agent to the radical-polymerizable thermosetting resin system may be about 55/45 to 95/5. Such a separator is suitable for fuel cell (in particular, solid polymer-type fuel cell), and can be produced with advantageous for commercial production.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a resin composition useful as a separator of a solid polymer-type fuel cell, a separator formed with the resin composition, and a process for producing the separator.

BACKGROUND OF THE INVENTION

[0002] A solid polymer-type fuel cell comprises a solid polymer electrolytic membrane composed of an ion exchange membrane (a polymer membrane having ion conductivity) such as perfluorocarbonsulfonic acid in which a sulfonic acid group is introduced into a fluorocarbon backbone such as a polytetrafluoroethylene backbone, two electrodes disposed on both sides of the electrolytic membrane, separators with grooves for supplying a gas such as hydrogen gas and oxygen gas to each electrode, and two current collectors disposed on backside of these separators.

[0003] Among these constituting members, the separator is required to have gas-imperviousness, low electrical resistance (electrical conductivity), resistance to sulfuric acid, and high mechanical strength. Traditionally, there is studied a method for molding a plate member made of titanium or graphite by a mechanical processing such as a cutting processing. However, this process lacks mass-productivity and it is difficult to carrying out on industrial scale.

[0004] Moreover, Japanese Patent Application Laid-Open No. 334927/1998 (JP-10-334927A) discloses a separator of a solid polymer-type fuel cell obtained by molding a resin composition which comprises a carbon powder, a thermosetting resin (phenolic resin, polyimide resin, epoxy resin, furan resin) by means of a resin molding process. However, the slow hardening of a phenolic resin used as the thermosetting resin results in the low productivity. For example, in Example 10 of the patent literature, post-hardening for 10 hours or more is required. Moreover, a gas such as water vapor generates as accompanied with hardening the phenolic resin so that warp forms in the hardened material and gas-imperviousness is deteriorated.

[0005] Further, Japanese Patent Application Laid-Open No. 267062/1992 (JP-4-267062A) discloses a gas separator for a fuel cell composed of stainless-steel or copper. However, although industrial productivity is high by the metal material, cell properties significantly lower due to deterioration of the material.

SUMMARY OF THE INVENTION

[0006] Thus, an object of the present invention is to provide a separator suitable for a fuel cell (in particular, solid polymer-type fuel cell) and a process capable of producing the separator with industrial advantageous.

[0007] Another object of the present invention is to provide a separator for a solid polymer-type fuel cell having gas-imperviousness, low electrical resistance, durability(especially, resistance to an acid such as resistance to sulfuric acid), and high mechanical strength, and a process for producing the separator with ease and effective.

[0008] Still another object of the present invention is to provide a separator of a solid polymer-type fuel cell with high dimensional accuracy, and a process for producing the separator with high molding accuracy.

[0009] A further object of the present invention is to provide a resin composition suitable for the above separator.

[0010] The inventors of the present invention found that, by using an electroconductive agent and a radical-polymerizable thermosetting resin in combination, a separator for a fuel cell which has not only material properties but also industrial productivity required of a separator can be obtained. The present invention was accomplished based on the above findings.

[0011] That is, the resin composition for a separator of a fuel cell of the present invention comprises an electroconductive agent and a radical-polymerizable thermosetting resin system. The radical-polymerizable thermosetting resin system may comprise at least a radical-polymerizable resin (especially, a radical-polymerizable resin and a radical-polymerizable diluent). From viewpoints of resistance to acid (e.g., resistance to sulfuric acid), mechanical properties and moldability, a vinyl ester-series resin (in particular, a vinyl ester-series resin in which (meth)acrylic acid is added to a bisphenol-type epoxy resin) is preferred as the radical-polymerizable resin. It is preferred for crosslinking that the double bond equivalent of the radical-polymerizable resin is about 200 to 1,000 (preferably about 200 to 800). It is preferred from the viewpoint of temperature for using a separator that the hardened radical-polymerizable thermosetting resin system has a glass transition temperature of 120 °C or more. The radical-polymerizable diluent may comprise at least an aromatic vinyl compound (especially, styrene). The weight ratio of the electroconductive agent to the radical-polymerizable thermosetting resin system may be about 55/45 to 95/5. The electroconductive agent preferably comprises a carbon powder. The resin composition may comprise a carbon powder, a radical-polymerizable vinyl ester-series resin having a plurality of α, β-ethylenically unsaturated double bonds, and a monomer having α,β-ethylenically unsaturated double bond, and the weight ratio of the vinyl ester-series resin to the monomer may be about 100/0 to 20/80, and the weight ratio of the carbon powder to the total amount of the vinyl ester-series resin and the monomer

may be about 55/45 to 95/5. The resin composition further comprises a low-profile agent (in particular, a thermoplastic resin such as a styrenic thermoplastic elastomer, a saturated polyester-series resin, and a vinyl acetate-series polymer). The amount of the low-profile agent may be about 0.1 to 30 parts by weight relative to 100 parts by weight of the radical-polymerizable thermosetting resin system.

[0012] The present invention also includes a separator for a solid polymer-type fuel cell formed with the resin composition (e.g., carbon separator). The separator is excellent in gas-imperviousness and durability. Moreover, the resin composition has excellent moldability. Therefore, the present invention also includes a process for producing the separator (e.g., carbon separator) by molding the resin composition by means of a resin molding method. Moreover, in the process, the resin composition may be kneaded with a pressure kneader and molded.

[0013] Incidentally, in the specification, the term "radical-polymerizable thermosetting resin system" means a resin composition comprising at least a radical-polymerizable resin, and is also used to include a resin composition comprising the radical-polymerizable resin and a radical-polymerizable diluent (monomer). Moreover, the term "radical-polymerizable resin" means a polymeric or oligomeric compound having a radical-polymerizable unsaturated bond, and the term "radical-polymerizable diluent" means a monomeric compound (monomer) having a radical-polymerizable unsaturated bond.

DETAILED DESCRIPTION OF THE INVENTION

[Electroconductive agent]

[0014] As the electroconductive agent (or electrically conductive agent), a variety of components such as carbon powders (a conventional artificial or synthetic graphite powder, expanded graphite powder, natural graphite powder, coke powder, electroconductive carbon black), carbon fibers and metal powders can be employed as far as the above component mainly contributes to decline electric resistance of the separator. These electroconductive agents can be used singly or in combination. Powder electroconductive agent such as carbon powder is usually employed. Since the electroconductive agent is tightly packed, a powder in which the grain size is adjusted, or a powder which is previously surface-treated can be also employed.

[0015] The average (mean) particle size of the electroconductive agent (in particular, carbon powder) can not specify unconditionally because of having a close relevancy to the ratio of the radical-polymerizable thermosetting resin system, but is usually about 10 nm to 100 μm, preferably about 20 nm to 80 μm and more preferably about 1 to 50 μm.

[Radical-polymerizable thermosetting resin]

[0016] It is sufficient that the radical-polymerizable thermosetting resin system comprises at least a radical-polymerizable resin, and the radical-polymerizable thermosetting resin system may comprise a radical-polymerizable resin alone. As the radical-polymerizable resin, there may be mentioned a resin or an oligomer having a α, β-ethylenically unsaturated bond (a polymerizable unsaturated bond), for example, vinyl ester-series resins, unsaturated polyester-series resins, urethane (meth)acrylates, polyester (meth)acrylates and the like. These radical-polymerizable resins can be used singly or in combination. The radical-polymerizable resin usually has a plurality of α, β-ethylenically unsaturated bonds.

(1) Vinyl ester-series resin

[0017] The vinyl ester-series resin (e.g., epoxy (meth)acrylate) is a ring-opening and addition reaction product of an epoxy group with a carboxyl group of a compound having a α, β-ethylenically unsaturated bond, and is an oligomer having a α, β-ethylenically unsaturated bond such as (meth)acryloyl group at its terminal position. The vinyl ester-series resin includes, for example, a reaction product of a compound having one or more epoxy groups in a molecule with an ethylenically unsaturated compound having a carboxyl group such as an unsaturated monobasic acid.

[0018] The compound having one-or more epoxy groups in a molecule includes epoxy resins, compounds having epoxy group and (meth)acryloyl group in a molecule.

[0019] As epoxy resin, there may be mentioned glycidyl ether-type epoxy resins, glycidyl ester-type epoxy resins, alicyclic epoxy resins in which a double bond of cycloalkene ring such as cyclohexene ring is epoxidated, glycidyl amine-type epoxy resins, copolymerization-type epoxy resins and the like.

[0020] As the glycidyl ether-type epoxy resin, there may be mentioned bisphenol-type epoxy resin [e.g., epoxy resins having a bis(hydroxyphenyl)C_{1-10}alkane backbone such as bisphenolA-type, bisphenolF-type and bisphenolAD-type epoxy resins, bisphenolS-type epoxy resin], novolak-type epoxy resins (e.g., phenolnovolak-type, cresol-novolak type epoxy resins), aliphatic epoxy resins (e.g., hydrogenated bisohenolA-type resin, propyleneglycol mono- or diglycidyl ether, pentaerythritol mono- to tetraglycidyl ether), monocyclic epoxy resins (e.g., resorcine glycidyl ether), heterocyclic

epoxy resins (e.g., triglycidylisocyanurate having a triazine ring, hydantoin-type epoxy resin having a hydantoin ring), tetrakis(glycidyloxyphenyl)ethane and the like.

[0021] As the glycidylester-type epoxy resin, there may be mentioned glycidyl esters of carboxylic acids (especially, polycarboxylic acid), for example, diglycidyl phthalate, diglycidyl terephthalate, dimethylglycidyl phthalate, diglycidyl tetrahydrophthalate, diglycidyl hexahydrophthalate and the like.

[0022] As the alicyclic epoxy resin, there may be mentioned, for example, alicyclic epoxy acetal, alicyclic diepoxy adipate, alicyclic dipoxy carboxylate, vinylcyclopentadiene dioxide, vinylcyclohexene mono- or dioxide and the like.

[0023] As the glycidyl amine-type epoxy resin, there may be mentioned reaction products of amines (particularly polyamines) and epichlorohydrine, for example, tetraglycidyldiaminodiphenylmethane, triglycidylaminphenol, diglycidylaniline, diglycidyltoluidine, and the like.

[0024] As copolymerization-type epoxy resin, there may be mentioned, for example, a copolymer having a bisphenolA backbone and a bisphenolF backbone.

[0025] These epoxy resins may be halogenated epoxy resins having a halogen atom (e.g., bromine, chlorine). Incidentally, Japanese Patent Application Laid-Open No. 110948/1997 (JP-9-110948A) refers to an epoxy resin which is a commercially available.

[0026] The epoxy equivalent of the epoxy resin varies according to the particle size of the electroconductive agent such as carbon powder, and is not particularly limited and is 50 to 5,000 g/eq, preferably about 100 to 1,000 g/eq, more preferably about 150 to 500 g/eq (in particular, about 170 to 250 eq/g).

[0027] As the compound having epoxy group and (meth)acryloyl group in a molecule, there may be mentioned C_{1-4}alkylglycidyl (meth)acrylate such as glycidyl (meth)acrylate and methylglycidyl (meth)acrylate, (meth) acryloyloxyC_{4-6}alkenylene oxide such as 4-(meth)acryloyloxymethylcyclohexene oxide and the like.

[0028] Among these epoxy group-containing compounds, glycidylether-type epoxy resins, epoxy resins having a saturated or unsaturated hydrocarbon ring or heterocycle, in particular, bisphenol-type epoxy resin are preferred. The bisphenol-type epoxy resin (e.g., bisphenolA-type epoxy resin) is preferred since the ratio of the electroconductive agent can be increased due to its low viscosity from a viewpoint of resistance to acid (resistance to sulfuric acid). Moreover, the bisphenol-type epoxy resin is used so that the moldability of resin composition improved due to the above properties and the mechanical strength of molded article can be enhanced.

[0029] As the ethylenically unsaturated compound having a carboxyl group such as an unsaturated monobasic acid, there may be mentioned, for example, unsaturated monocarboxylic acids such as (meth)acrylic acid, crotonic acid and cinnamic acid, a reaction product of a polybasic acid anhydride with a compound having (meth)acryloyl group and an active hydrogen atom (e.g., hydroxyl group) in a molecule.

[0030] As the polybasic acid anhydride, there may be mentioned aliphatic dicarboxylic acid anhydrides such as maleic anhydride and succinic anhydride, aromatic dicarboxylic acid anhydrides such as phthalic anhydride, tetrahydrophthalic anhydride and hexahydrophthalic anhydride. As the compound having (meth)acryloyl group and an active hydrogen atom, there may be mentioned monohydroxy compounds [e.g., hydroxyC_{2-6}alkyl (meth)acrylates such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate and hydroxybutyl (meth)acrylate], reaction products of (meth)acrylic acid with a polyhydric alcohol [e.g., trimethylolpropane di(meth)acrylate, pentaerythritol tri(meth)acrylate, glycerin di(meth)acrylate].

[0031] Among ethylenically unsaturated compounds having a carboxyl group, unsaturated monocarboxylic acids, in particular, (meth)acrylic acid are preferred.

[0032] The molar ratio of the ethylenically unsaturated compound having a carboxyl group to the epoxy compound is carboxyl group/epoxy group = 0.8/1 to 1.2/1, preferably about 0.9/1 to 1.1/1.

[0033] The ring-opening and addition reaction of epoxy group with carboxyl group can be carried out under conventional conditions and, for example, the reaction may be carried out in the presence of a tertiary amine such as trialkylamine and dimethylbenzylamine or a phosphine such as triphenylphosphine as a catalyst at a reaction temperature of about 80 to 150 °C for 1 to 10 hours.

[0034] Moreover, in case that there is need for increasing the viscosity of resin during molding, a vinyl ester-series resin capable of increasing its viscosity with an alkali may be used, and may be obtained by adding a polybasic carboxylic anhydride to a hydroxyl group generated by reacting epoxy group with carboxyl group to generate a carboxyl group.

(2) Unsaturated polyester-series resin

[0035] A reaction product of a unsaturated polybasic acid with a polyol and if necessary, a saturated polybasic acid can be used as the unsaturated polyester-series resin. As the polybasic acid, a dicarboxylic acid or a reactive derivative thereof is usually used.

[0036] As the unsaturated polybasic acid, there may be mentioned a C_{4-6}aliphatic unsaturated polybasic acid or an anhydride thereof such as maleic anhydride, fumaric acid, maleic acid and itaconic acid.

[0037] As the saturated polybasic acid, there may be mentioned C_{2-10}aliphatic saturated polybasic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, suberic acid, and sebacic acid; C_{8-12}aromatic polybasic acids or anhydrides thereof such as isophthalic acid, terephthalic acid, phthalic acid, phthalic anhydride, tetrachlorophthalic anhydride, trimellitic acid and pyromellitic acid; C_{8-10}alicyclic polybasic acid or anhydride thereof such as 1,4-cyclohexanedicarboxylic acid, tetrahydrophthalic acid, chlorendic acid (HET acid) and nadic anhydride.

[0038] The proportion of the unsaturated polybasic acid is, for example, about 25 to 100 mol%. preferably about 30 to 100 mol%, more preferably about 50 to 100 mol% relative to the whole polybasic acid.

[0039] As the polyol, there may be mentioned C_{2-12}alkylene glycols (e.g., ethylene glycol, propylene glycol, butanediol, 1,5-pentadiol, 3-methyl-1,5-pentadiol, 1,6-hexanediol, neopentyl glycol), polyoxyC_{2-4}alkylene glycol (e.g., diethylene glycol, triethylene glycol, dipropylene glycol, triphenylene glycol), aromatic diols (e.g., bisphenolA, bisphenolA-C_{2-4}alkylene oxide adducts).

[0040] The esterification reaction can be carried out by a conventional method and, for example, can be conducted at an atmosphere of an inert gas in the presence of an esterification catalyst under an ordinary pressure or reduced pressure and an temperature of about 70 to 120 °C with removing formed water from the reaction system.

[0041] The molar ratio of the polybasic acid to the polyol is usually carboxyl group of polybasic acid/hydroxyl group of polyol = about 0.7/1 to 1.3/1, preferably about 0.8/1 to 1.2/1.

(3) Urethane (meth)acrylate

[0042] A reaction product of a polyurethane oligomer having an isocyanate group at its terminal position with the above hydorxyC_{2-6}alkyl (meth)acrylate can be employed as the urethane (meth)acrylate.

[0043] A conventional polyurethane oligomer obtainable with the use of excess amount of diisocyanate component relative to diol component can be used as the polyurethane oligomer. The polyurethane oligomer includes, for example, a reaction product of a diisocyanate component (e.g., an aromatic diisocyanate such as tolylenediisocyanate and diphenylmethanediisocyanate, an araliphatic diisocyanate such as xylylenediisocyante and tetramethylxylylenediisocyanate, an alicyclic diisocyanate such as isophoronediisocyanate, an aliphatic diisocyanate such as hexamethylenediisocyanate) with a diol component (e.g., C_{2-12}alkylene glycols, polyether diols such as polyoxyC_{2-4}alkylene glycols, polyester diols, polycarbonate diols).

[0044] The molar ratio of hydroxyl group to isocyanate group of the urethane oligomer is hydroxyl group/isocyanate group = about 0.7/1 to 1.2/1, preferably about 0.8/1 to 1.1/1, more preferably about 0.9/1 to 1/1.

[0045] The urethanated reaction is carried out by a conventional method and, for example, is conducted in the presence of a catalyst at an atmosphere of an inert gas at a temperature of about 50 to 100 °C.

(4) Polyester (meth)acrylate

[0046] A reaction product of a polyester oligomer having hydroxyl group or carboxyl group at its terminal position with (meth)acrylic acid, hydroxyC_{2-6}alkyl(meth)acrylate, or glycidyl (meth)acrylate can be used as polyester (meth) acrylate.

[0047] The polyester oligomer may be linear, or branched formed by using a polyhydric alcohol (e.g., glycerin) in addition to the monomer constituting the unsaturated polyester. The polyester oligomer can be produced by adjusting the ratio of the polybasic acid (in particular, saturated polybasic acid) and the polyol and conducting the esterification reaction mentioned above.

[0048] The amount to be used of (meth)acrylic acid, hydroxyC_{2-6}alkyl(meth)acrylate, or glycidyl (meth)acrylate is about 0.8 to 1.2 mol, preferably about 0.9 to 1.2 mol relative to 1 mol of hydroxyl group or carboxyl group of the polyester oligomer.

[0049] Among the radical-polymerizable resins, vinyl ester-series resins, in particular, reaction products of bisphenol-type epoxy resin with (meth)acrylic acid are preferred because of having high resistance to acid (e.g. , resistance to sulfuric acid) and mechanical properties, and excellent mold-flowability.

[0050] The double bond equivalent in the radical-polymerizable resin is about 200 to 1,000, preferably about 200 to 800, more preferably about 200 to 650. When the double bond equivalent is too small, a hardened material having the extremely high crosslinking density is formed and it is difficult that the hardened material is used industrially due to its fragility. On the other hand, when the double bond equivalent is too large, crosslinking can not occur sufficiently and it is difficult to obtain the sufficient heat resistance and mechanical properties.

[0051] Incidentally, the acid value of the radical-polymerizable resin such as a vinyl-ester-series resin, an unsaturated polyester-series resin, a polyurethane (meth)acrylate and a polyester (meth)acrylate is about 0.1 to 5 mgKOH/g, preferably about 0.5 to 3 mgKOH/g.

(Radical-polymerizable diluent)

[0052] It is preferred that the radical-polymerizable resin is diluted with the use of a reactive diluent having at least one double bond (especially α, β-ethylenically unsaturated bond), i.e., radical-polymerizable diluent in a molecule in order to decrease its viscosity and adjust the crosslinking density.

[0053] As the radical-polymerizable diluent, there may be mentioned unsaturated carboxylic acids such as (meth) acrylic acid, crotonic acid and cinnamic acid; C_{1-12}alkyl esters of unsaturated carboxylic acids such as methyl (meth) acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate and dodecyl (meth)acrylate; glycidyl esters of unsaturated carboxylic acids such as glycidyl (meth)acrylate ; hydroxyC_{2-8}alkyl ester of unsaturated carboxylic acids such as 2-hydroxyethyl (meth)acrylate; nitrogen-containing monomer such as (meth) acrylamide, (meth)acrylonitrile and vinyl pyrrolidone ; aromatic vinyl compounds such as styrene, vinyl toluene, divinyl benzene and p-t-butylstyrene ; C_{2-8}alkylene glycol esters of unsaturated carboxylic acids such as ethylene glycol di (meth)acrylate, 1,4-butandiol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate ; polyoxyalkylene glycol ester of unsaturated carboxylic acids such as diethylene glycol di(meth)acrylate ; polyfunctional (meth)acrylates such as trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate and pentaerythritol tetra(meth)acrylate. Among these diluents, the aromatic vinyl ester, in particular, styrene is preferred from the viewpoints of moldability and economy. These diluents can be used in singly or in combination.

[0054] The aromatic vinyl compound (in particular, styrene) has higher copolymerizability with the radical-polymerizable resin (e.g., vinyl ester-series resin) compared with (meth)acrylic monomers (diluent) so that properties of molded articles (e.g., mechanical strength) can be enhanced. Further, the aromatic vinyl compound has high dilution efficiency (i.e., can easily lower viscosity) so that the moldability can be improved even when used in small amount. Furthermore, the aromatic vinyl compound is superior to other diluents (e.g., acrylic diluents) in chemical resistance. Therefore, it is preferred that the radical-polymerizable diluent comprises at least the aromatic vinyl compound (in particular, styrene).

[0055] The weight ratio of the radical-polymerizable resin to the radical-polymerizable diluent can be usually selected within the range of about 100/0 to 20/80, and is about 95/5 to 20/80, preferably about 90/10 to 40/60, more preferably about 90/10 to 55/45. In order to show higher heat resistance, it is advantageous that the amount of the diluent is decreased.

[0056] The weight ratio of the electroconductive agent to the radical-polymerizable thermosetting resin system is about 55/45 to 95/5, preferably about 60/40 to 95/5, more preferably about 65/35 to 92/8. When the amount of the electroconductive agent is too small, the electroconductivity (electrically conductive) can not be improved. When the amount of the electroconductive agent is too large, the mold-flowability becomes insufficient so that molding operation becomes to be difficult.

[0057] Incidentally, the weight ratio of the electroconductive agent to the radical-polymerizable resin is about 55/45 to 95/5, preferably about 60/40 to 95/5, more preferably about 65/35 to 95/5.

[Low-profile agent]

[0058] In the resin composition of the present invention, it is preferred for the purpose of inhibiting warp and curing shrinkage of the molded article and improving the dimensional accuracy that the low-profile agent (or an agent capable of imparting low shrinkage to a molded article) is contained. In general, since the radical-polymerizable thermosetting resin system shrinks during molding and tends to cause unevenness and warp, the dimensional accuracy is sometimes deteriorated. In this case, dimensional accuracy of molded article can be improved by the low-profile agent.

[0059] As the low-profile agent (or low-shrinking agent), there may be mentioned non-polymerizable resins such as polyester-series resins (e.g., saturated aromatic polyester-series resins such as polyethylene terephthalate and polybutylene terephthalate, saturated aliphatic polyester-series resins such as polyethylene adipate, polybutylene adipate and polybutylene sebacate, copolymerizable saturated polyester-series resins having a polyoxyethylene unit), acrylic resins [e.g., homo- or copolymers having a C_{1-10}alkyl ester of (meth)acrylic acid as a monomer component such as polymethyl methacrylate], vinyl acetate-series polymers (e.g., polyvinyl acetate, ethylene-vinyl acetate copolymer), styrenic resins [e.g., homo- or copolymers of a styrenic monomer such as polystyrene, copolymers of styrene and a copolymerizable monomer such as styrene-(meth)acrylic acid block copolymer, styrene-(meth)acrylate block copolymer and styrene-vinyl acetate block copolymer, crosslinked polystyrene], polyolefinic resins [e.g., polyethylene, ethylene-(meth)acrylic acid copolymer, ethylene-(meth)acrylate copolymer), thermoplastic elastomer (e.g., styrenic thermoplastic elastomer, olefinic thermoplastic elastomer, polyester-series thermoplastic elastomer, polyvinyl chloride-series thermoplastic elastomer, polyurethane-series thermoplastic elastomer). Among these low-profile agents, styrenic thermoplastic elastomers [e.g., styrene-diene-series copolymer (e.g., styrene-butadiene block copolymer, styrene-isoprene block copolymer or hydrogenated thereof)], saturated polyester-series resins, vinyl acetate-series polymers (e. g., polyvinyl acetate) are preferred.

[0060] These low-profile agents can be used singly or in combination. The amount of the low-profile agent is about

0.1 to 30 parts by weight, preferably about 0.5 to 25 parts by weight, more preferably about 1 to 20 parts by weight relative to 100 parts by weight of the radical-polymerizable thermosetting resin system. When the amount of the low-profile agent is small, the dimensional accuracy tends to be deteriorated. When the amount is too large, properties such as thermal resistance are declined.

[0061] The number average molecular weight of the low-profile agent can be selected according to the species of the thermosetting resin, and is not particularly limited, but is usually about 1, 000 to 10 $\times$ 10^5, preferably about 2,000 to 5 x 10^5, more preferably about 3,000 to 5 x 10^5.

[0062] When a resin composition containing the low-profile agent is molded, the shrinking rate of the molded article is decreased to not more than 0.15 %, preferably not more than 0.1 %, more preferably not more than 0.05 % so that the dimensional accuracy can be improved.

[0063] To the radical-polymerizable thermosetting resin system may be added a rubber component in order to improve the property of the separator as a hardened material such as tenacity and impact resistance. As the rubber component, there may be mentioned liquid rubbers or modified thereof [e.g., acrylonitrile-butadiene rubber (NBR) having the terminal carboxyl group, NBR having the terminal epoxy group, NBR having the terminal vinyl group], microfine particulate rubbers (e.g., crosslinked acrylic microfine particle). The amount of the rubber component is usually about 1 to 30 parts by weight relative to 100 parts by weight of the radical-polymerizable thermosetting resin system.

[Curing agent and curing promoter]

[0064] The resin composition of the present invention can be easily hardened by adding a conventional curing agent and if necessary, a conventional curing promoter used for hardening the radical-polymerizable thermosetting resin system.

[0065] As the curing agent, there may be mentioned organic peroxides, for example, aliphatic peroxides (e.g., methyl ethyl ketone peroxide, t-butyl peroxy2-ethylhexanoate, di-t-butyl peroxide, lauroyl peroxide), aromatic peroxides (e.g., benzoyl peroxide, dicumyl peroxide, cumene hydroperoxide, t-butyl peroxybenzoate), alicyclic peroxides (e.g., cyclohexanone peroxide). The amount of the curing agent is about 0.1 to 5 parts by weight, preferably about 0.5 to 3 parts by weight, more preferably about 1 to 3 parts by weight relative to 100 parts by weight of the radical-polymerizable thermosetting resin system.

[0066] As the curing promoter, there may be mentioned metal salts (e.g., transition metal salts such as cobalt naphthenate and cobalt octanoate), amines (e.g., tertiary amines such as dimethylaniline, diethylaniline), acetylacetone. The amount of the curing promoter is about 0.01 to 3 parts by weight, preferably about 0.05 to 2 parts by weight, more preferably about 0.1 to 2 parts by weight relative to 100 parts by weight of the radical-polymerizable thermosetting resin system.

[Other additives]

[0067] If necessary, to the resin composition of the present invention may be also added a conventional additive such as a filler (e.g., aluminum hydroxide, glass powder, calcium carbonate, talc, silica, clay, glass balloon), polymerization inhibitor (e.g., hydroquinone, t-butylcatechol), reinforcing fiber (e.g., glass fiber, carbon fiber), release agent (e.g., metal soap such as calcium stearate, zinc stearate, silicone or fluorene-containing organic compound, phosphoric acid-series compound), thickner (e.g., oxide or hydroxide of magnesium or calcium).

[Glass transition temperature of the hardened material]

[0068] It is preferred that the glass transition temperature of the hardened material of the radical-polymerizable thermosetting resin system comprising at least radical-polymerizable resin (i.e., the radical-polymerizable resin alone or a resin composition comprising the radical-polymerizable resin and the radical-polymerizable diluent) is 120 °C or more (especially, about 140 to 200 °C). Since a solid polymer-type fuel cell is sometimes used at upper temperature of not less than 100 °C, it is preferred that a separator is in the form of glass and retains sufficient elasticity around this temperature.

[Method for molding the resin composition and its use]

[0069] The resin composition of the present invention can be molded by a conventional molding method because of its high flowability and moldability. The resin molding method includes, for example, a conventional method for molding resin such as injection molding and compression molding. More concretely, the resin composition can be injected into the given mold and applied with heat and pressure to obtain a molded article. In particular, by utilizing a radical reaction, not only generation of warp can be inhibited but also an uniform molded article can be obtained with short time. Further,

since the molded article can be obtained by a method for molding a resin, there is no need for cutting process and a groove as a gas-passageway can be formed precisely. Incidentally, deairing or defoaming of the resin composition may be carried out in order to obtain uniform molded article.

[0070] Incidentally, when the resin composition is kneaded with the use of a conventional kneader, a powder or coarse particulate compound is sometimes formed. On the other hand, when the resin composition is kneaded with the use of a pressure kneader (or a kneader capable of kneading under pressure), a viscous or clay-like uniform compound can be obtained. In particular, even when the electroconductive agent is packed in high concentration, an uniform compound having excellent flowability can be prepared. Thus, when a compound is molded by a pressure kneader, a molded article, which is smooth surface without unevenness and has the excellent outer appearance without any defects such as cavity, can be obtained. Further, mechanical properties such as compression strength and bending or flexural strength of the molded article can be improved.

[0071] In the pressure kneader, the pressure is not particularly limited as far as an uniform compound is obtained, and is about 0.1 to 10 kgf/cm^2 (about 9.8 x 10^3 to 9.8 x 10^5 Pa), preferably about 0.3 to 8 kgf/cm^2, more preferably about 0.5 to 8 kgf/cm^2 (in particular, about 1 to 8 kgf/cm^2).

[0072] The blade shape of the pressure kneader includes Banbury type, Sigma blade, single curve and the like. Among these shapes, banbary-type is preferred. The rotation number of the blade is not particularly limited, and is about 5 to 150 rpm, preferably about 10 to 120 rpm. The kneading temperature is not particularly limited, and is about room temperature to about 100 °C, preferably about room temperature to about 80 °C (e.g., about room temperature to 50 °C). Incidentally, the kneading can be carried out at suitable atmosphere, and is usually conducted in air. Moreover, the kneading is usually carried out under shading.

[0073] In the present invention, clay-like or viscous compound can be obtained by kneading the resin composition with the pressure kneader. The viscosity at 25 °C of the compound during molding is about 1 x 10^2 to 1 x 10^6 Pa·s, preferably about 1 x 10^3 to 1 x 10^6 Pa·s, more preferably about 1 x 10^3 to 1 x 10^5 Pa·s (determined by Heripas viscosimeter). Incidentally, by means of kneading with a pressure kneader, the mechanical strength and thermal conductivity can be enhanced, and in particular, thermal conductivity can be improved even when using a non-electroconductive material (e.g., low-profile agent). Thus, a molded article without any defects can be obtained.

[0074] The hardened material of the resin composition of the present invention shows gas-imperviousness, low electrical resistance, resistance to acid (resistance to sulfuric acid), and high mechanical strength, and can be easily molded by a resin molding method. Thus, the resulting molded article can be used in a variety of applications such as electric or electronic device parts, and in particular, is useful for a separator of a solid polymer-type fuel cell equipped with a solid polymer electrolytic membrane.

[0075] The separator is usually in the form of plate and has a groove for gas-passageway supplying with hydrogen gas or oxidant gas (e.g., oxygen-containing gas such as oxygen gas). The thickness of the separator is about 1 to 10 mm (especially about 2 to 5 mm), and one or more grooves may be formed in the separator.

[0076] Since the hardened molded article made of the resin composition of the present invention can contain large amounts of an electroconductive agent, the molded article has high electroconductivity, high mechanical strength, low gas-perviousness, excellent durability (especially, resistance to an acid such as resistance to sulfuric acid), and high dimensional accuracy. Further, since the resin composition of the present invention can be molded by a resin molding method, and is a compound having an excellent flowability, the resin composition is also superior in moldability. Thus, the resin composition of the present invention is suitable as a material for a separator of a fuel cell, especially solid polymer-type fuel cell.

EXAMPLES

[0077] Hereinafter, the present invention will further be described based on the following examples.

Example 1

[0078] To a four-neck flask equipped with a stirrer, a condenser, a nitrogen-inlet, and thermometer were charged 374 g of bisphenolA-type epoxy resin (manufactured by Toto Kasei Co. Ltd., epototoYD128, epoxy equivalent 187 g/eq), 172 g of methacrylic acid, 0.2 g of triphenylphosphine, 0.1 g of hydroquinone as a thermal polymerization inhibitor, and reacted for 8 hours at 120 °C to obtain 546 g of vinyl ester resin having an acid value of 1.8 mgKOH/g. The vinyl ester resin was diluted with 364 g of styrene monomer to obtain a resin composition.

[0079] The resin composition (180 g) was surely kneaded with 450 g of artificial graphite powder (manufactured by SEC Co. Ltd., SGL25, average particle size of 25 μm), 850 g of artificial graphite powder (manufactured by SEC Co. Ltd., SGB20, average particle size of 20 μm) and 3.6 g of t-butylperoxybenzoate (manufactured by Nippon Yushi Co. Ltd., TBPB), and after deairing, cured in a plate mold (300 x 300 x 8 mm) under 50 kg/cm^2 (4.9 x 10^6 Pa) at 150 °C for 2 minutes to obtain the molded plate.

Example 2

[0080] A molded plate was obtained in the similar manner to Example 1 except for using 280 g of the resin composition of Example 1 and 1100 g of artificial graphite powder (SGB20).

Example 3

[0081] A molded plate was obtained in the similar manner to Example 1 except for using 450 g of the resin composition of Example 1, 500 g of artificial graphite powder (SGL) and 200 g of artificial graphite powder (SGB).
[0082] Incidentally, when 1.5 g of t-butylperoxybenzoate (manufactured by Nippon Yushi Co. Ltd., TBPB) was added to the used vinyl ester-series resin composition, the glass transition temperature of the hardened one was 160 °C.
[0083] In the plates obtained by Examples 1 to 3, the following properties were evaluated. The results are shown in Table 1.

(Electric resistance)

[0084] The electric resistance was determined according to JIS R 7202.

(Bending strength)

[0085] The bending strength was determined according to JIS K 7203 of three point bending method.

(Gas-perviousness)

[0086] The gas-perviousness was determined with nitrogen gas and was shown by the following formula

Nitrogen gas-perviousness = (perviousness amount of nitrogen gas) x (thickness of test piece)/(time) x (cross section) x (differential pressure) [unit : cm^2/sec atm]

(Resistance to sulfuric acid)

[0087] The outer appearance of the plate after immersing for 1 month at 50 °C to 50 weight % of sulfuric acid was evaluated according to the following criteria.

A : change in the outer appearance is not visibly recognized
B : change in the outer appearance is visibly recognized

Table 1

	Electric resistance [$\mu\cdot\Omega\cdot cm$]	Bending strength [kg/mm^2]	Gas-perviousness [$cm^2/sec\cdot atm$]	Resistance to sulfuric acid
EX. 1	1000	4.8	$<10^{-6}$	A
EX. 2	1200	5.4	$<10^{-6}$	A
EX. 3	19600	6.5	$<10^{-6}$	A

[0088] As apparent from Table 1, the plate formed with the resin composition of the present invention has low electric resistance, high bending strength, low gas-perviousness and excellent resistance to sulfuric acid.

Example 4

[0089] The resin composition (280 g) obtained in Example 1 was kneaded with 330 g of artificial graphite powder (manufactured by SEC Co. Ltd., SGL10, average particle size of 10 μm), 770 g of artificial graphite powder (manufactured by SEC Co. Ltd., SGL25, average particle size of 25 μm) and 5.6 g of t-butylperoxybenzoate (manufactured by Nippon Yushi Co. Ltd., TBPB) by a conventional kneader, a molded plate was obtained in similar manner to Example 1. Incidentally, the kneaded compound is coarse particulate.

Example 5

[0090] The resin composition (224 g) obtained in Example 1 was kneaded with 28 g of styrene-butadiene block copolymer (D-KX410CS, Shell JSR Elastomer), 330 g of artificial graphite powder (manufactured by SEC Co. Ltd., SGL10, average particle size of 10 μm), 770 g of artificial graphite powder (manufactured by SEC Co. Ltd., SGL25,

average particle size of 25 μm) and 5.6 g of t-butyl peroxybenzoate (manufactured by Nippon Yushi Co. Ltd., TBPB) by a conventional kneader, a molded plate was obtained in similar manner to Example 1. Incidentally, the kneaded compound is coarse particulate.

Example 6

[0091] A plate is molded in similar manner to Example 5 except for kneading with the use of a pressure kneader under a pressure of 3.92 x 10^6 Pa (4 kgf/cm^2), and at 40 °C and 50 rpm. Incidentally, the kneaded compound is clay-like.

Example 7

[0092] A plate is molded in similar manner to Example 6 except for using saturated polyester resin (manufactured by Toyobo Co. Ltd., vylon330) in lieu of styrene-butadiene copolymer. Incidentally, the kneaded compound is clay-like.

[0093] In the plates obtained in Examples 4 to 7, the above mentioned electric resistance, bending strength and resistance to sulfuric acid were determined, and further, thermal conductivity, shrinking rate, specific gravity and warp were determined according to the following methods.

(Thermal conductivity)

[0094] Two plates (50 mm x 50 mm x 10 mm) were piled, and the thermal conductivity was determined by Hotdisk method (a method for determining thermal conductivity by relatively comparing with an international standard material according to NIST of United States) at 23 °C with the use of thermal property analyzer (manufactured by TPA-501 type (Kyoto Denshi Kogyo Co. Ltd.)). Incidentally, the determination was carried out three times and the thermal conductivity was represented as an average value.

(Shrinking rate)

[0095] The linear shrinking of a plate (300 mm x 300 mm x 5 mm) was determined.

(Warp)

[0096] Plates (300 mm x 300 mm x 1 mm) were allowed to stand at 23 °C under 50 %RH for 1 day. An error in thickness of each plate was less than 0.1 mm. Each plate was disposed on an even glass plate, the distance between each of four corners (edges) of the plate and the glass plate surface was determined when the center point of the plate was fixed. The warp was represented as the average value of the distances.

Table 2

	Electric resistance [μ·Ω·cm]	Bending Strength [kg/mm^2]	Gas-perviousness [cm^2/sec·atm]	Thermal conductivity [W/(m·K)]	Shrinkage Rate [%]	Specific gravity	Warp
Ex. 4	1000	5.5	$<10^{-6}$	29	0.16	1.90	14
Ex. 5	1000	6.1	$<10^{-6}$	31	0.05	1.84	4.1
Ex. 6	1000	6.5	$<10^{-6}$	36	0.04	1.83	3.2
Ex. 6	1000	6.7	$<10^{-6}$	35	0.04	1.83	3.6

[0097] As apparent from Table 2, by containing the low-profile agent, shrinking and warp of the molded article can be inhibited. Moreover, when kneading is carried out by the pressure kneader, a molded article having high bending strength, high thermal conductivity, low shrinking and low warp can be obtained.

Claims

1. A resin composition for a separator of a fuel cell, which comprises an electroconductive agent and a radical-polymerizable thermosetting resin system.

2. A resin composition according to Claim 1, wherein the radical-polymerizable thermosetting resin system comprises at least a radical-polymerizable resin.

3. A resin composition according to Claim 1, wherein the radical-polymerizable thermosetting resin system comprises a radical-polymerizable resin and a radical-polymerizable diluent.

4. A resin composition according to Claim 2, wherein the radical-polymerizable resin comprises a vinyl ester-series resin.

5. A resin composition according to Claim 2, wherein the radical-polymerizable resin comprises a vinyl ester-series resin in which (meth)acrylic acid is added to a bisphenol-type epoxy resin.

6. A resin composition according to Claim 2, wherein the double bond equivalent of the radical-polymerizable resin is 200 to 1,000.

7. A resin composition according to Claim 1, wherein the hardened radical-polymerizable thermosetting resin system has a glass transition temperature of 120 °C or more.

8. A resin composition according to Claim 3, wherein the radical-polymerizable diluent comprises at least an aromatic vinyl compound.

9. A resin composition according to Claim 1, wherein the weight ratio of the electroconductive agent to the radical-polymerizable thermosetting resin system is 55/45 to 95/5.

10. A resin composition according to Claim 1, wherein the electroconductive agent comprises a carbon powder.

11. A resin composition according to Claim 1, which comprises a carbon powder, a radical-polymerizable vinyl ester-series resin having a plurality of α, β-ethylenically unsaturated double bonds, and a monomer having α, β-ethylenically unsaturated double bond, wherein the weight ratio of the vinyl ester-series resin to the monomer is 100/0 to 20/80, and the weight ratio of the carbon powder to the total amount of the vinyl ester-series resin and the monomer is 55/45 to 95/5.

12. A resin composition according to Claim 1, which comprises a carbon powder, a vinyl ester-series resin formed by adding a (meth)acrylic acid to a bisphenol-type epoxy resin and a radical-polymerizable diluent comprising at least a styrene, wherein the double bond equivalent of the vinyl ester-series resin is 200 to 800.

13. A resin composition according to Claim 1, which further comprises a low-profile agent.

14. A resin composition according to Claim 13, wherein the low-profile agent comprises at least one member selected from the group consisting of a styrenic thermoplastic elastomer, a saturated polyester-series resin, and a vinyl acetate-series polymer.

15. A resin composition according to Claim 13, wherein the amount of the low-profile agent is 0.1 to 30 parts by weight relative to 100 parts by weight of the radical-polymerizable thermosetting resin system.

16. A separator for a solid polymer-type fuel cell formed with the resin composition recited in Claim 1.

17. A process for producing the separator recited in Claim 16 which comprises molding the resin composition recited

in Claim 1 by a resin molding method.

18. A process according to Claim 17, which comprising kneading the resin composition recited in Claim 1 with a pressure kneader and molding the kneaded one.

19. A process according to Claim 18, wherein the pressure in the pressure kneader is 0.1×10^5 to 10×10^5 Pa.

20. Use of a resin composition for a separator of a fuel cell, wherein the resin composition comprises an electroconductive agent and a radical-polymerizable thermosetting resin system.

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(54) **Separator for solid polymer type fuel cell and process for producing the same**

(57) A separator for solid polymer-type fuel cell is produced by molding the resin composition which comprises an electroconductive agent and a radical-polymerizable thermosetting resin system by a resin molding method. The electroconductive agent comprises a carbon powder. The radical-polymerizable thermosetting resin system may comprise a radical-polymerizable resin (especially, a vinyl ester-series resin) and a radical-polymerizable diluent. It is preferred that the double bond equivalent of the radical-polymerizable resin may about 200 to 1,000 and that the hardened radical-polymerizable thermosetting resin system has a glass transition temperature of 120 oC or more. The weight ratio of the electroconductive agent to the radical-polymerizable thermosetting resin system may be about 55/45 to 95/5. Such a separator is suitable for fuel cell (in particular, solid polymer-type fuel cell), and can be produced with advantageous for commercial production.

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EUROPEAN SEARCH REPORT

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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TECHNICAL FIELDS SEARCHED (Int.Cl.7)
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(54) Title: INJECTION MOLDABLE CONDUCTIVE AROMATIC THERMOPLASTIC LIQUID CRYSTALLINE POLYMERIC COMPOSITIONS

(57) Abstract

A method for making a shaped article or a shaped article having a volume resistivity of less than 10^{-2} ohm–cm with a desired combination of properties and processibility in an injection moldable composition. In particular the shaped articles formed include injection molded bipolar plates as current collectors in fuel cell applications.

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TITLE

INJECTION MOLDABLE CONDUCTIVE AROMATIC THERMOPLASTIC LIQUID CRYSTALLINE POLYMERIC COMPOSITIONS

FIELD OF INVENTION

The present invention relates to an injection moldable electrically conductive composition comprising aromatic thermoplastic liquid crystalline polymers (LCPs), electrically conductive articles made therefrom, and the injection molding process for making them. The compositions of the invention are useful in a wide variety of applications including electrochemical devices such as battery current collectors, high efficiency electromagnetic/radio frequency interference shielding, and electrostatic dissipative packaging and equipment housings. The present invention is particularly useful in fuel cells.

BACKGROUND OF THE INVENTION

In the current state of the art, a typical fuel cell comprises the elements shown in Figure 1. A membrane/electrode assembly (MEA), 10, comprising a membrane separator, 11, and catalyst coatings, 12, on either side thereof, and two (2) gas diffusion backing sheets, 20, are sealed by gaskets, 30, between two (2) electronically conductive graphite plates, 40. The plates often serve a multiple role as current collectors conveying electrons to the external load via electrical connections not shown, as mechanical supports for the other fuel cell components, and as gas and water distribution networks via a pattern of flow fields inscribed upon the surfaces thereof, 50. Gas and water inputs and outputs are generally integral with the graphite plate, but are not shown. The graphite plates normally serve as the interface between adjacent cells in a stack. The plates are known variously as current collectors, flow fields, and bipolar (or monopolar) plates. For further information, see, for example, Ullmann's Encyclopedia of Industrial Chemistry, 5th ed. Vol. 12A, pp. 55ff, VCH, New York, 1989.

Because of its multiple role, the bipolar plate has a number of requirements to meet. The plate must have good electrical conductivity, good mechanical or structural properties and high chemical stability in the chemically reactive fuel cell environment. In addition because of its gas distribution role it must be made of a gas impermeable material and be formed with complex gas delivery channels across its surface.

In the current practice of the art, graphite is the material of choice for bipolar plates because of its high electrical conductivity, high strength and immunity to corrosion. However, it is brittle, expensive, and requires expensive machining to produce. The brittleness of graphite necessitates its use in ca. six (6)

mm thick slabs which adds both weight and bulk to the fuel cell, thus driving down its power density (kW/l or kW/kg) in use.

Carbon/graphite filled thermoplastic polymers have long been identified as a promising alternative to graphite in bipolar plates. In principle, conductive, reinforced thermoplastic polymer compositions can be molded directly into complex, intricate shaped components using low cost, high-speed molding processes. In addition, these more ductile materials will enable the development of new stack designs because moldable plastics offer much greater flexibility to the form of fuel cell components. Unfortunately, this potential has not been realized in the art despite numerous attempts to do so.

Electrically conductive thermoplastic polymer compositions providing volume resistivities of 10^{-3}-10^{-2} ohm-cm are known in the art, and are of particular interest in the production of fuel cell current collectors.

US-A 3,945,844 to Nickols discloses polymer/metal composites. Polysulfone, polyphenylene sulfide, polyphenylene oxide, acrylonitrilebutadiene-styrene copolymer are combined in a variety of ways with stainless steel, silver, gold, and nickel. The amount of either metal powders or fillers or both, in the polymer/metal composite varies from 50 to 80 weight % percent. Resistivity levels as low as 10^{-3} ohm-cm are reported.

US-A-4,098,967 to Biddick et al. provides a bipolar plate formed of thermoplastic resin filled with 40-80% by volume finely divided vitreous carbon. Plastics employed in the compositions include polyvinylidene fluoride and polyphenylene oxide. The plates are formed by compression molding dryblended compositions and possess specific resistance on the order of 0.002 ohm-cm. Compression molded bipolar plates from solution blends of graphite powder and polyvinylidene fluoride are disclosed in US-3,801,374 to Dews et al. The plate so formed has a density of 2.0 g/cc and volume resistivity of 4×10^{-3} ohm-cm.

US-A-4,214,969 to Lawrance discloses a bipolar plate fabricated by pressure molding a dry mixture carbon or graphite particles and a fluoropolymer resin. The carbon or graphite are present in a weight ratio to the polymer of between 2.5:1 and 16:1. For polymer concentrations in the range of 6-28% by weight, volume resistivity is in the range of 1.2-3.5×10^{-3} ohm-in.

In US- A-4,339,322 to Balko et al., the physical strength of the compression molded composite of US-A-4,214,969 was improved by substituting carbon fibers or other fibrous carbon structures for some of the graphite powder. Typical composition includes 20% (by weight) polyvinylidene fluoride (PVDF), 16% (by weight) carbon fiber, and graphite powder. The dry mixture was

blended, then pressure molded into plates. The volume resistivity is in the range of 1.9×10^{-3} to $3.9\ 10^{-3}$ ohm-in at a binder/resin loading levels of 7-26 wt %.

US-A-4,554,063-85 to Braun et al. discloses a process for fabricating cathode current collectors. The current collector consists of graphite (synthetic) powder of high purity, having particle sizes in the range from 10 (micron) to 200 (micron) and carbon fibers which are irregularly distributed therein and have lengths from 1 mm to 30 mm, the graphite powder/carbon fiber mass ratio being in the range from 10:1 to 30:1. The binder/resin used is polyvinylidene fluoride. For producing the current collector, the binder is dissolved in, for example, dimethylformamide. Graphite powder and carbon fibers are then added and the resulting lubricating grease-like mass is brought to the desired thickness by spreading on a glass plate and is dried for about 1 hour at about 50°C. The plates were also formed by casting, spreading, and extrusion.

US-A-5,582,622 to Lafollette discloses bipolar plates comprising a composite of long carbon fibers, a filler of carbon particles and a fluoroelastomer.

Also known in the art is the use of metal-coated, particularly nickel-coated chopped graphite fibers to form conductive polymer compositions. In order to reduce fiber attrition by compounding, the prior art discloses employing a thermoplastic resin-impregnated bundle of nickel-coated graphite fibers which are directly injection moldable with a thermoplastic matrix resin with only a preliminary dry-blending step. See for example Kiesche, "Conductive Composites Find Their Niche," Plastics Technology, November 1985, P. 77ff; Murthy et al, "Metal Coated Graphite Fiber Structural Foam Composites," Fourteenth Annual Structural Foam Conference and Parts Competition, The Society of the Plastics Industry, Inc., April 1986, PP 86ff. Use of wider gates and flow channels in molding machines processing graphite fibers is disclosed for example in International Encyclopedia of Composites, S. Lee, ed. pp 474ff, VCH publishers, 1990. Also disclosed therein is the enhancement of conductivity realized by orientation of high aspect ratio conductive fibers in the polymer matrix during the molding process.

Methods for forming resin-impregnated graphite fibers which are also applicable to metal-coated graphite are known in the art. Some of these methods are disclosed in "Graphite Fiber Composites (Electrochemical Processing)" by J. Iroh in Polymeric Materials Encyclopedia, J. C. Salamone, ed., pp. 2861ff, CRC Press 1996.

The art hereinabove cited is directed to replacing pure metal or graphite components which require extensive machining to be formed into finished articles

with moldable compositions based upon thermoplastic polymer resins which require less, post-molding machining to form the finished article.

The problem in realizing the advantages of molded thermoplastic polymer parts has been related to the inverse relationship between concentration of conductive filler on the one hand and processibility and mechanical properties on the other. In practice, as shown in the art hereinabove cited, quantities of conductive filler required to achieve the 10^{-2} ohm-cm resistivity goal in fuel cells result in products with limited practical utility. This is particularly true in regard to the formation of current collectors in fuel cell applications.

It is desirable to achieve a combination of properties and processibility in an injection moldable composition without the limitation on practical utility. Another advantage desired is the reduction in cost of forming finished articles such as current collectors in comparison to conventional methods.

SUMMARY OF THE INVENTION

Briefly stated, and in accordance with one aspect of the present invention, there is provided a process for fabricating a shaped article having a volume resistivity of less than 10^{-2} ohm-cm, the process comprising:

combining an injection moldable aromatic thermoplastic liquid crystalline polymer resin and a composition comprising nickel-coated graphite fibers impregnated with a non-liquid-crystalline thermoplastic binder resin, to form a mixture at a temperature below the melting point of the thermoplastic liquid crystalline polymer resin, the graphite fibers being of a length of less than 2 cm and comprising about 5 to about 50% by weight of the mixture, and the binder resin comprising about 0.1 to about 20% by weight of the graphite;

feeding the mixture to an injection molding machine wherein the thermoplastic liquid crystalline polymer resin is melted and fed in the molten state to a mold; cooling the mold to a temperature at which the thermoplastic liquid crystalline polymer in the mixture no longer flows; and,removing the molded mixture from the mold.

Pursuant to another aspect of the invention, there is provided a shaped article having a volume resistivity of less than 10^{-2} ohm-cm comprising about 50 to about 95% by weight of an aromatic liquid crystalline polymer about 5 to about 50% by weight of a nickel-coated graphite fiberof a length less than 2 cm, and about 0.1 to about 20% by weight with respect to the weight of the graphite fiber of a non-liquid-crystalline thermoplastic binder resin.

Pursuant to another aspect of the invention, there is provided a process for fabricating an electrically conductive shaped article, the process comprising: combining an injection moldable aromatic thermoplastic liquid crystalline

polymer resin in the form of particles characterized by a mean particle size of less than 1500 micrometers with a graphite filler to form a mixture at a temperature below the melting point of the thermoplastic liquid crystalline polymer resin, the graphite filler being present in a concentration of about 5% to about 80% by weight of the total mixture; feeding the mixture to an injection molding machine wherein the aromatic thermoplastic liquid crystalline polymer resin is melted and fed in the molten state to a mold; cooling the mold to a temperature at which the resin in the mixture no longer flows; and, removing said molded mixture from the mold.

BRIEF DESCRIPTION OF THE FIGURES

Other features of the present invention will become apparent as the following description proceeds and upon reference to the Figures, in which:

Figure 1 is a schematic illustration of a typical fuel cell; and

Figure 2 is a schematic illustration of a molded bipolar plate with fluid distribution channels.

DETAILED DESCRIPTION OF THE INVENTION

The compositions of the present invention provide a novel balance among conductivity, processibility, and structural properties. Surprisingly, it was found in the practice of the invention that injection molded plaques having excellent strength and stiffness can be produced with electrical volume resistivity in the range of 10^{-3}-10^{-2} ohm-cm. The plaques so formed are suitable for use as current collectors in fuel cells at thicknesses in the range of about 0.2 to about 10 mm. with a preferred thickness of 1-3 mm. The combination of properties achieved by these plaques compares favorably with the machined graphite plaques which represent the current state of the art in fuel cell development. However, the present invention provides the advantage of a significantly reduced cost in the process of forming the shaped articles.

In a preferred embodiment of the present invention, the necessary balance of properties to permit direct injection molding of complex shaped articles with excellent structural properties, processibility, and volume resistivity of 10^{-2} ohm-cm or less is achieved. Despite the teachings of the prior art , and the obvious economic incentive to develop injection molded current collectors to replace the current expensive method, no satisfactory injection molded current collectors have been produced prior to the present invention. It is well known in the art that processibility and structural properties deteriorate as the amount of filler incorporated into a polymeric matrix is increased. In the art as hereinabove described, in order to achieve the volume resistivity of 10^{-2} ohm-cm or less required for practical application to fuel cells, the requisite quantity or loading of

conductive fiber and other fillers into the selected polymer matrices resulted in melt viscosities too high to permit injection molding, and such poor structural properties such as ductility, flexural strength, and impact strength that only excessively thick plaques could be employed without exhibiting structural failure in use.

The term "thermoplastic" as used herein refers to the thermoplastic liquid crystalline polymer resin suitable for the practice of the present invention that is melt processible according to conventional methods known in the art for melt processing plastics such as screw extrusion and injection molding.

In the present invention, the easy moldability of aromatic thermoplastic liquid crystalline polymers allows formation of conductive shaped articles of complex shape and thin walls and sufficient loading of conductive fillers affords excellent conductivity. The excellent chemical resistance of molded aromatic thermoplastic liquid crystalline polymers combined with the as-molded complex shapes makes the process of the present invention particularly well-suited for the fabrication of bipolar plates useful in fuel cells.

Furthermore, an embodiment of the present invention provides an injection moldable composition comprising an injection moldable aromatic thermoplastic liquid crystalline polymerthermoplastic thermoplastic liquid crystalline polymer resin, and a conductive graphite filler, which is fed to an injection molding machine wherein the aromatic thermoplastic liquid crystalline polymerthermoplastic thermoplastic liquid crystalline polymer is melted, the graphite filler is dispersed within the polymer melt so formed during the advance of the injection molding screw, and the molten resin composition is fed to a mold wherein it is solidified and then ejected as a solid shaped article.

In a preferred embodiment of the present invention, the ingredients of the composition are dry mixed prior to feeding. Dry mixing may be accomplished by any convenient means such as tumbling. Preferably, the composition also comprises a dispersing agent, and such other additives as may be desired or required to improve processibility or end-use properties.

Aromatic thermoplastic liquid crystalline polymers suitable for the practice of the present invention include those described in U.S. Patents 3,991,013; 3,991,014; 4,011,199; 4,048,148, 4075,262;4083829; 4118372;4122070; 4,130,545; 4,153,779; 4,159,365;4,161,470; 4,169,933; 4,184,996;4,189,549; 4,219,461;4,232,143;4232,144; 4,245,082; 4,256,624; 4,269,964; 4,272,625; 4,370,466;4,383,105;4,447,592;4,522974;4,617,369;4,664,972;4,684,712; 4,727,129;4,727,131;4,728,714;4,749769;4,762,907;4,778,927;4,816,555; 4,849,499;4,851,496;4,851,497;4,857,626;4,864,013;4,868,278;4,882,410;

4,923,947; 4,999,416; 5015721;5,015,722;5,0254,082;5,086,158; 5,102,935; 5,110,896; 5,143,956.

Useful aromatic thermoplastic liquid crystalline polymers include polyesters, poly(ester-amides), poly(ester-imides), and polyazomethines. Especially useful are aromatic thermoplastic liquid crystalline polymers that are polyesters or poly(ester-amides). It is also preferred in these polyesters and poly(ester-amides) that at least about 50 %, more preferably about 75% of the bonds to ester or amide groups, i.e., the free bonds of -C(O)O- and -C(O)NR^1- where R^1 is hydrogen or hydrocarbyl, be to carbons atoms which are part of aromatic rings.

In a preferred embodiment of the present invention, the polyesters or poly(ester-amides) are made from monomers such as one or more aromatic dicarboxylic acid such as isophaltic acid, terephtalic acid, 4,4-bibenzoic acid, 2,6-napthalene dicarboxylic acid, one or more aromatic dihydoxy compounds such as hydroquinone, a substituted hydroquinone such as methylhydroquinone, t-butylhydroquinone, and chlorohydroquinone, resorcinol, 4,4'-biphenol, 2,6-napthalenediol, and 2,7-napthalenediol, one or more aromatic hydroxyacids such as 3-hydroxybenzoic acid, 4-hydroxybenzoic acid, and 6-hydroxy-2-napthoic acid and (in the case of poly(ester-amides)) one or more aromatic diamines such as p-phneylenediamine or m-phenylenediamine.

Included within the definition herein of an aromatic thermoplastic liquid crystalline polymer is a blend of 2 or more aromatic thermoplastic liquid crystalline polymers, or a blend of an aromatic thermoplastic liquid crystalline polymer with one or more non-aromatic thermoplastic liquid crystalline polymers wherein the aromatic thermoplastic liquid crystalline polymer is the continuous phase.

In one embodiment of the present invention, an aromatic thermoplastic liquid crystalline resin is combined with a conductive, metal-coated, preferably nickel-coated, graphite fiber, formed into pellets by the adhesive action of a thermoplastic resin binder. In the process of the invention, the aromatic thermoplastic liquid crystalline resin is preferably dry mixed, as by tumbling, with the metal-coated graphite fiber pellets to form a coarse homogeneous mixture. The mixture is fed to the feed throat of an injection molding machine and the resins melt as the resin mixture is conveyed along the flights of the screw while the action of the screw causes the fibers to disperse within the aromatic thermoplastic liquid crystalline resin melt. The molten dispersion is fed to a mold in which the melt hardens to form a shaped article which is then ejected from the mold.

In a preferred embodiment of the present invention, the shaped article formed according to the process of the invention is a bipolar plate having fluid-flow channels molded into the surface thereof being suitable for use in hydrogen or direct methanol fuel cells with little or no post molding finishing required. Suitable conductive fibers are graphite fibers, preferably metal coated graphite fibers, and most preferably nickel-coated graphite fibers. The length of the graphite fibers is less than ca. 1", preferably 0.125-0.5", and the diameter is in the range of about 5 to about 40 micrometers, preferably about 5 to about 15 micrometers. While any degree of metal coating is an improvement over uncoated graphite fibers, a metal coating level of about 20% to about 70% by weight of the total weight of the metal-coated fiber plus thermoplastic resin binder is preferred while approximately 45%-60% is most preferred. Because of the combination of chemical stability, low density, excellent performance, and low cost, nickel is the preferred coating metal.

In the preferred embodiment of the present invention, nickel-coated graphite fibers are present in the composition of the invention at concentrations in the range of about 5% to about 50%, preferably about 10% to about 40% by weight.

In the preferred embodiment of the invention, the thermoplastic resin binder represents about 0.1 to about 20% by weight, preferably about 5 to about15% by weight of the total nickel-coated graphite fiber composition prior to mixing into the composition of the invention. The most preferred polymeric binder is a low melting polyamide copolymer or terpolymer.

The following discussion is provided for the purpose of illustrating a preferred embodiment of the invention and not for limiting same. Because of limitation in both residence time and screw design in injection molding machines, it is believed that considerable benefit accrues when the time available for dispersion of the metal-coated graphite fiber in the molten resin matrix is maximized. Pursuant to that goal, it is preferable that the thermoplastic binder resin become fluid at a lower temperature than that at which the aromatic thermoplastic liquid crystalline resin melts, thus, ensuring that the dispersion of the fiber will be well-under way while the aromatic thermoplastic liquid crystalline resin is melting.

The thermoplastic binder resin may or may not be useful as a dispersing agent. Alternatively, it may be desirable to add a dispersing agent to the composition.

The thermoplastic resin binder may be deposited on to the fibers of the invention by any means known in the art including melt impregnation, solution

impregnation, in-situ polymerization of dispersed monomer, and electrodeposition. No one means, known in the art, is preferred over another.

Aromatic thermoplastic liquid crystalline polymers are manufactured and commercially available as pellets ca. 0.125" in diameter. It is found surprisingly in the practice of the present invention that conductivity is improved when aromatic liquid crystalline pellets are subject to size attrition to form particles having a mean particle size of less than 1500 μm, preferably less than 1000 μm, prior to combining with a conductive graphite filler.

In a further embodiment of the present invention, an aromatic thermoplastic liquid crystalline resin having a mean particle size of less than 1500 μm, preferably less than 1000 μm, is combined with a conductive graphite filler. In the process of the present invention, the aromatic thermoplastic liquid crystalline resin is preferably dry mixed, as by tumbling, with the graphite filler to form a coarse homogeneous mixture. The mixture is fed to the feed throat of an injection molding machine and the aromatic thermoplastic liquid crystalline polymer melts as it is conveyed along the screw flights, and the action of the screw causes the filler to disperse within the aromatic thermoplastic liquid crystalline resin melt. The molten dispersion is fed to a mold in which the melt hardens to form a shaped article which is then ejected from the mold.

The conductive graphite filler is present in the composition of the invention at concentrations in the range of about 5% to 80%, preferably about 30 to 70% by weight, most preferably 30 to 50% by weight. Suitable graphite fillers include powdered graphite, such as Thermocarb® graphite powder from Conoco, Inc., more preferably a graphite fiber, such as pitch based graphite fibers available from Conoco, Inc., still more preferably, a metal-coated graphite fiber, most preferably a nickel-coated graphite fiber such as hereinabove described.

Attrition of the particle size of the aromatic thermoplastic liquid crystalline resin pellets may be accomplished according to the following procedure: A rotary cutter or grinder, such as an ABBE cutter (Model Number: 000 Laboratory Rotary Cuttter serial no. 49491, Abbe Engineering Company, Brooklyn, NY 11211), is equipped with a metal screen having holes 0.060 inches (0.15 cm) in diameter. A beaker is filled with aromatic thermoplastic liquid crystalline resin pellets and immersed in liquid nitrogen and held for ca. two minutes after the liquid has stopped boiling. After immersion in the liquid nitrogen, the beaker of pellets is removed and the pellets fed to the moving blades of the cutter. Frequent clearing of the cutter is necessary because only ca. 50% of the resin pellets are actually effectively cut, leaving the cutter

contaminated with a buildup of warmed pellets. The residual pellets may be recycled to the cutter after further immersion in liquid nitrogen.

It is found in the practice of the invention that when pellets of nickel-coated graphite of ca. 3.2 mm in size and larger are combined with the powdered thermoplastic liquid crystalline resin of less than 1.5 mm in size, and particularly less than 1.0 mm in size, some separation of components occurs during feeding to the injection molding machine. Some loss in homogeneity within and among resulting molded parts may result. It is therefore, desirable to take additional measures to ensure that the components remain well mixed on a macroscopic scale while feeding. This may be accomplished by employing nickel-coated graphite fibers having a smaller aspect ratio so that the pellets formed therefrom may have smaller dimensions. Another method is to adapt stuffer box technology known for feeding extruders to feeding injection molding machines. Still another method is to maintain mixing even as the material is fed into the screw of the injection molding machine. These, and other methods known in the art, may be employed, alone or in combination, to maintain homogeneity in the embodiments of the invention in which a considerable size mismatch occurs in the materials being fed.

To improve the homogeneity of the dispersion of the conductive filler into the aromatic thermoplastic liquid crystalline polymer, it may be desirable to incorporate into the compositions, formed according to the process of the present invention, a dispersing aid. The dispersing aid can be of any type known in the art to be effective in enhancing the dispersibility of metal or graphite fibers in polymeric melts. The dispersing aid may be crystalline or non-crystalline, and may be normally liquid at room temperature. In the present invention, the dispersing aid is required to be immobile in the composition at room temperature. For a liquid dispersing aid, the liquid must be immobilized by adsorption or absorption onto the fiber. Suitable dispersing aids include low molecular weight species such as fatty acids, silanes, difunctional oligomers and so forth. Dispersing aids may also be polymeric in nature, such as the thermoplastic resin binder incorporated into the nickel-coated graphite fiber pellets which are preferred for use in the present invention. The choice of dispersing aid is also governed by compatibility with the matrix polymer. Compatibility is largely an empirical determination. A compatible dispersing aid is one that will cause the fiber to disperse within the polymeric matrix, whereas a non-compatible dispersing aid doesn't cause dispersion but instead causes the fiber to form isolated clumps.

The composition of the present invention may contain such other additives as may be required to improve processibility or properties. In particular, in the practice of the present invention the addition of ca. 5-20% by weight carbon black to the composition provides a desirable improvement in conductivity with relatively small degradation of processibility or structural properties. Preferred is a highly structured carbon black such as Printex XE from Degussa, Black Pearl 2000 from Cabot or Ketjenblack EC300J from Akzo Nobel.

It is important in the present invention that the ingredients be subject to as little shearing force as possible because shearing force associated with melt mixing and extrusion normally performed to form filled polymeric compositions results in degradation of the conductivity performance. Thus all steps in the process of the present invention should be performed with an eye toward keeping shear forces low.

While any means known in the art for mixing at low shear is suitable, in the practice of the present invention simple dry tumbling of the ingredients works well. In the process of the present invention, the mixture so formed is fed to a conventional injection molding machine where the polymers undergo melting, and are conveyed to the mold followed by cooling and ejection. The injection moldable composition of the invention is suitable for use on any injection molding machine which provides the limited melt shear necessary for dispersion of the fibers in the matrix polymer melt. While a wide range of mold and runner geometries may be employed, it is found advantageous to reduce the degree of shear to which the melt is subject by employing large diameter gates and runners.

For the purposes of the present invention, premixing the dry or unmelted ingredients at low shear includes simply feeding the separate ingredients directly to the feed hopper of the injection molding machine such as by employing controlled rate-of- weight-loss feeders where the mixture is made *in situ* within the feed throat of the injection molding machine.

This invention enables the production of thinner (e.g., all the molded samples in the Examples section below are 1/8" (~3.2 mm) thick, the target thickness range for bipolar plates in fuel cells is about 1 to about 3 mm.), lighter, and lower cost conductive articles while significantly reducing or eliminating the need for the costly machining steps employed at the current state of the art. The articles of the invention exhibit volume resistivity of ca. 10^{-2} ohm-cm or less. In the preferred embodiment, current collectors having complex gas flow networks, highly suitable for use in fuel cells may be directly injection molded, requiring little or no finishing prior to use.

Reference is now made to the following specific embodiments for the purpose of illustrating the invention and for limiting same.

EXAMPLES

A description of the materials employed in the examples hereinbelow cited is provided in Table 1.

TABLE 1

Description of Materials

Name	Description	Manufacturer	Resin Melting Point	Product Form
Zenite® HX8000	Aromatic liquid crystalline Aromatic Polyester,	DuPont Company, Wilmington DE	~240-260°C	Resin pellets
PP1-1204-Ni60 and PP1-1208-Ni60	Resin Impregnated Nickel-coated Graphite Fibers (with 60w% nickel coating)	Composite Materials, LLC, Mamaroneck, NY USA	~232°C	1/4" and 1/2" fibers in pellet form-pellet diamter (~1/16")-12000 fibers per pellet (~7-8 micrometer), typical fiber aspect ratio – 300-1000
PP1-1204-NiCu40	Resin Impregnated Nickel-Copper Coated Graphite Fibers with ~35% copper and about 5% nickel	Composite Materials, LLC, Mamaroneck, NY USA	~232°C	1/4" and 1/2" fibers in pellet form-pellet diamter (~1/16")-12000 fibers per pellet (~7-8 micrometer), typical fiber aspect ratio – 300-1000
Thermocarb® CF300	Graphite Powder	Conoco, Ponca City, OK USA		Particle size 45 –300 micrometer
Mesophase pitch-based graphite fiber	Graphite Fiber	Conoco, Ponca City, OK USA		Fiber length ca. 1mm

The nickel-coated graphite fibers were supplied in the form of 12,000 fiber pellets containing 5-15 wt-% of a low melting polyamide binder with a melting point 232°C. The fibers further consisted of 60% by weight nickel and 25-35% by weight graphite. The fibers were provided in 1/4" and 1/2" lengths.

Drying conditions applicable to the materials cited in the examples cited hereinbelow are as shown in Table 2.

TABLE 2

Drying Conditions

Material	Drying Temperature (°C)	Duration at Temperature (hours)	Other
Zenite® HX8000	105	=12	hopper dryer under N2
Nickel-coated graphite fibers	220	=4	oven dried under N2
Thermocarb® CF300	--	--	used as received
Mesopitch Graphite Fibers			used as received

In all examples injection molding was effected utilizing a 180 ton injection molding machine (Nissei Manufacturing, Nagano, Japan). The parts formed were 3"x 6"x 0.125" and 4"x4"x0.125" flat plaques.

All the volume resistivity measurements were done on the flat molded plaques using a four point probe (ref: "Electrical Resistivity Measurements of Polymer Materials" by A. R. Blythe in Polymer Testing 4 (1984) 195-200). Six (6) measurements were done on each side of the sample and the average of the measurement is reported as the volume conductivity number in the following examples.

EXAMPLE 1

2730 g of HX8000 (dried at 105°C for 12 hrs) was dry blended by tumbling with 910 g ach of 1/4" and 1/2" long Nickel coated Graphite Fibers pellets. The blended mixture was injection molded at the following conditions.

Melt Temperature:	320°C
Mold Temperature:	30-70°C
Injection pressure:	703 kg/cm^2
Injection speed:	2.5-5 cm/sec
Screw Speed:	50-75 RPM
Set Injection time (max):	14 sec
Set Curing Time (max):	18 sec
Set Cycle Start Time (max):	1 sec
Back Pressure:	0 kg/cm^2

The volume resistivity was found to be about 2.0×10^{-3} ohm-cm.

Reference is now made to Figure 2 which shows a molded bipolar plate of Example 1 with fluid distribution channels, 100, molded therein.

EXAMPLE 2

3185 g of HX8000 was dry blended with 682 g each of 1/4" long and 1/2" long Nickel coated Graphite Fibers pellets. The blended mixture was injection molded at the following conditions.

Melt Temperature:	320°C
Mold Temperature:	80-87°C
Injection pressure:	492 kg/cm^2
Injection speed:	2.5-5 cm/sec (variable in cycle)
Screw Speed:	50-75 RPM
Set Injection time (max):	14 sec
Set Curing Time (max):	18 sec.
Set Cycle Start Time (max):	1 sec.
Back Pressure:	0 kg/cm^2
Shot Size:	54%

The volume resistivity was found to be about 1.0×10^{-2} ohm-cm.

COMPARATIVE EXAMPLE 1

2730 g of HX8000 and 6370 g of Thermocarb CF300 graphite Powder were melt compounded under vacuum in a Welding Engineers (King of Prussia, PA) 20 mm counter-rotating twin screw extruder. The polymer was fed into the first zone while the graphite was fed down stream after the polymer had melted. Screw speed was 125-150 rpm, and throughput was ca. 4550-6800 g. Die temperature was ca. 290-300°C. The extruded strand was chopped into ca. 0.125" pellets.

About 1360 g of formulation thus compounded was dryblended first with 910 g of additional HX8000 and then dry blended with 455 g each of 1/2" long and 1/4" long Nickel Graphite Fibers pellets. The blended mixture was injection molded at the following conditions.

Melt Temperature:	320°C
Mold Temperature:	70-80°C
Injection pressure:	984 kg/cm^2
Injection speed:	2.5-5 cm/sec (variable in cycle)
Screw Speed:	50-75 RPM
Set Injection time (max):	14 sec
Set Curing Time (max):	18 sec

Set Cycle Start Time (max):	1 sec
Back Pressure:	0 kg/cm^2

The volume resistivity was found to be about 2.5×10^{-2} ohm-cm.

COMPARATIVE EXAMPLE 2

2730 g dryblended HX8000 with 1820 g of Copper (on Nickel coating) coated (about 45 wt. % metal on fiber basis) graphite Fibers pellets. Each pellet contains 12000 fibers held together with a nylon proprietary based binder (5-15 wt %-fiber basis).

The blended mixture was injection molded at the following conditions.

Melt Temperature:	320°C
Mold Temperature:	70-76°C
Injection pressure:	703 kg/cm^2
Injection speed:	2.5-5 cm/sec
Screw Speed:	50-75 RPM
Set Injection time (max):	14 sec
Set Curing Time (max):	18 sec
Set Cycle Start Time (max):	1 sec
Back Pressure:	0 kg/cm^2

The volume resistivity was found to be about 2.3×10^{-2} ohm-cm.

EXAMPLES 3-6 AND COMPARATIVE EXAMPLES 3-6

In Examples 3-6 and Comparative Examples 3-6 a comparison is drawn between the volume resistivity of flat plates molded from compositions comprising 3200 μm (0.125 inch) aromatic thermoplastic liquid crystalline resin pellets as received from the manufacturer, and compositions comprising 951 μm mean particle size cryogenically ground pellets.

The thermoplastic liquid crystalline resin powder was made by filling a 250 ml plastic beaker provided with holes in the bottom and fitted with a a wire handle with ca. 1/8" (3.2 mm) resin pellets, followed by immersion of the thus filled beaker into a large bath of liquid nitrogen contained in a Dewar flask. The beaker was kept in the liquid nitrogen for a period of two minutes following the cessation of active boiling of the liquid nitrogen. An ABBE rotary cutter provided with a metal screen having holes 0.060" (1.5 mm) was started with the hopper slide closed. Wearing a face shield and thermally insulated gloves, the resin filled beaker was removed from the liquid nitrogen and its contents dumped into the feed hopper of the cutter. The slide was opened and the pellets fell into the blades. In any given run, only about 50% of the pellets fed were ground up. It was therefore necessary to stop every third or fourth run to clean out residual, now-warmed pellets and recycle them through the process.

Size determination were done using a laser diffraction method employing a Malvern Mastersizer X manufactured Malvern Instruments Ltd, Malvern, UK.

Whether powdered or in pellet form, the Zenite 8000 thermoplastic liquid crystalline resin (available in 3.2 mm pellets from DuPont, Wilmington, DE) was dried for 12 hours at 105°C under nitrogen.

In all cases a 180 ton injection molding machine (Nissei Mftg., Nagano, Japan) was employed to form plaques of dimensions 3" x 6" x 0.125" or 4" x 4" x 0.125".

Results are tabulated in Table 3.

EXAMPLE 3

700 grams of the thermoplastic liquid crystalline resin powder was tumble-blended with 1300 grams of Thermocarb® CF300 graphite powder, the blend then fed immediately to the injection molding machine and molded under the following injection molding conditions:

Melt Temperature	320°C
Mold Temperature	150°C
Injection Pressure	1125 kg/cm^2
Injection Speed	5 cm/sec (variable in cycle)
Screw Speed	125-140 RPM
Set Injection Time (max)	30.0 sec.
Set Curing time (max)	60.0 sec.
Set Cycle Start time (max)	1 sec.
Back Pressure	0 kg/cm^2
Shot size	~40-60%.

EXAMPLE 4

The materials and conditions of Example 3 were repeated except that 600 grams of thermoplastic liquid crystalline resin powder were combined with 1400 grams of Thermocarb® CF300.

EXAMPLE 5

1050 grams of thermoplastic liquid crystalline resin powder was tumble blended with 1290 grams of Thermocarb® CF300 graphite powder and 660 grams of mesphase pitch based graphite fibers. The combination was fed immediately to an injection molding machine, and injection molded under the following injection molding conditions:

Melt Temperature	320°C
Mold Temperature	150°C
Injection Pressure	1335 kg/cm^2
Injection Speed	2.5-5 cm/sec (variable in cycle)

Screw Speed	100-125 RPM
Set Injection Time (max)	25.0 sec.
Set Curing time (max)	45.0 sec.
Set Cycle Start time (max)	1 sec.
Back Pressure	0 kg/cm^2
Shot size	~40-60%.

EXAMPLE 6

The materials and procedures of Example 5 were employed except that 990 grams of the graphite fiber was employed.

COMPARATIVE EXAMPLE 3

700 gms of dried Zenite 8000 pellets was dryblended by tumbling with 1300 gm of Thermocarb graphite powder CF300. The blended mixture was directly injection molded according to the following injection molding conditions:

Melt Temperature	320°C
Mold Temperature	150°C
Injection Pressure	1195 kg/cm^2
Injection Speed	2.5-5 cm/sec (variable in cycle)
Screw Speed	100-125 RPM
Set Injection Time (max)	20.0 sec.
Set Curing time (max)	30.0 sec.
Set Cycle Start time (max)	1 sec.
Back Pressure	0 kg/cm^2
Shot size	~40-60%

COMPARATIVE EXAMPLE 4

The materials and procedures of Comparative Example 3 were employed except that 600 grams of dried Zenite 8000 pellets was combined with 1400 grams of Thermocarb CF300.

COMPARATIVE EXAMPLE 5

1050 gms of dried Zenite 8000 pellets was dryblended by tumbling with 1290 gm of Thermocarb graphite powder CF300 and 660 gm of pitch based graphite fibers. The blended mixture was injection molded under the following injection molding conditions:

Melt Temperature	320°C
Mold Temperature	150°C
Injection Pressure	1195 kg/cm^2
Injection Speed	2.5-5 cm/sec(variable in cycle)
Screw Speed	100-125 RPM
Set Injection Time (max)	20.0 sec.

Set Curing time (max)	30.0 sec.
Set Cycle Start time (max)	1 sec.
Back Pressure	0 kg/cm^2
Shot size	~40-60%.

COMPARATIVE EXAMPLE 6

The materials and procedures of Comparative Example 5 were repeated except that 1050 grams of Zenite were combined with 990 grams of Thermocarb CF300 and 990 grams of pitch based graphite fibers.

TABLE 3

Volume Resistivity in Examples 4-8 and Comparative Examples 4-8

Example	**Vol. Resist (4pt. Probe)** ***ohm.cm***
Ex. 3	*0.18*
Comp. Ex. 3	0.21
Ex. 4	*0.12*
Comp. Ex. 4	0.15
Ex. 5	*0.18*
Comp. Ex. 5	0.27
Ex. 6	*0.18*
Comp. Ex. 6	0.32

IT IS CLAIMED:

1. A process for fabricating a shaped article having a volume resistivity of less than 10^{-2} ohm-cm, the process comprising:

combining an injection moldable aromatic thermoplastic liquid crystalline polymer resin and a composition comprising nickel-coated graphite fibers impregnated with a non-liquid-crystalline thermoplastic binder resin, to form a mixture at a temperature below the melting point of the thermoplastic liquid crystalline polymer resin, the graphite fibers being of a length of less than 2 cm and comprising about 5 to about 50% by weight of the mixture, and the binder resin comprising about 0.1to about 20% by weight of the graphite;

feeding the mixture to an injection molding machine wherein the thermoplastic liquid crystalline polymer resin is melted and fed in the molten state to a mold;

cooling the mold to a temperature at which the thermoplastic liquid crystalline polymer in the mixture no longer flows; and,

removing the molded mixture from the mold.

2. The process of Claim 1, wherein the nickel coated graphite fibers comprise about 10- about 40% by weight of the total composition.

3. The process of Claim 1, wherein the nickel-coated graphite fibers are of a diameter in the range of about 5- about15 micrometers.

4. The process of Claim 1, wherein the nickel-coated graphite fibers have a nickel-coating representing about 45%- about 60% or a total weight of the nickel-coated graphite fibers.

5. The process of Claim 1, wherein the aromatic thermoplastic liquid crystalline polymer is a polyester or a poly(ester-amide).

6. The process of Claim 5, wherein at least 50% of the bonds to ester or amide groups are to carbon atoms which are part of aromatic rings.

7. The process of Claim 6, wherein at least 75% of the bonds to ester or amide groups are to carbon atoms which are part of aromatic rings.

8. The process of Claim 1, wherein the binder resin comprises about 5%- about15% by weight of the graphite.

9. A shaped article having a volume resistivity of less than 10^{-2} ohm-cm comprising about 50- about 95% by weight of an thermoplastic aromatic liquid crystalline polymer and about 5% to about 50% by weight of a nickel- coated graphite fiber of a length less than 2 cm, and a non-liquid-crystalline thermoplastic resin.at a concentration of about 0.1%- about 20% by weight with respect to the weight of the graphite.

10. The shaped article of Claim 9, wherein the shaped article comprises about 10% to about 40% by weight of the nickel-coated graphite fiber.

11. The shaped article of Claim 9, wherein the nickel-coated graphite fiber is of a diameter in the range of about 5 to about15 micrometers.

12. The shaped article of Claim 9, wherein the nickel-coating represents about 45 to about 60% or the total weight of the nickel-coated graphite fiber.

13. The shaped article of Claim 9, wherein the aromatic thermoplastic liquid crystalline polymer is a polyester or a poly(ester-amide).

14. The shaped article of Claim 13, wherein at least 50% of the bonds to ester or amide groups are to carbon atoms that are part of aromatic rings.

15. The shaped article of Claim 14 wherein at least 75% of the bonds to ester or amide groups are to carbon atoms that are part of aromatic rings.

16. The shaped article of Claim 9, wherein the binder resin comprises about 5%- about15% by weight of the graphite.

17. The shaped article of Claim 9, comprising a form of a bipolar plate.

18. The shaped article of Claim 17, wherein the bipolar plate has a thickness in the range of about 0.1 to about 10 mm.

19. The shaped article of Claim 18, wherein the bipolar plate thickness is in the range of about 1 to about 3 mm.

20. The shaped article of Claim 17, further comprising fluid distribution channels inscribed upon the surface thereof.

21. A process for fabricating an electrically conductive shaped article, the process comprising:

combining an injection moldable aromatic thermoplastic liquid crystalline polymer resin in the form of particles characterized by a mean particle size of less than 1500 micrometers with a graphite filler to form a mixture at a temperature below the melting point of the thermoplastic liquid crystalline polymer resin, the graphite filler being present in a concentration of about 5% to about 80% by weight of the total mixture;

feeding the mixture to an injection molding machine wherein the aromatic thermoplastic liquid crystalline polymer resin is melted and fed in the molten state to a mold;

cooling the mold to a temperature at which the resin in the mixture no longer flows; and,

removing said molded mixture from the mold.

22. The process of Claim 21, wherein the thermoplastic liquid crystalline polymer resin particles are characterized by a mean particle size of less than 1000 micrometers.

23. The process of Claim 21, wherein the graphite filler comprises a graphite fiber.

24. The process of Claim 23, wherein the graphite filler comprises a fiber of a length less than 2 cm.

25. The process of Claim 23, wherein the graphite fiber further comprises a metal coating.

26. The process of Claim 25, wherein the metal coating is a nickel coating.

27. The process of Claim 26, wherein the nickel coated graphite fiber comprises about 10% to about 40% by weight of the total composition.

28. The process of Claim 26 wherein the nickel-coated graphite fiber are of a diameter in the range of 5 to 15 micrometers.

29. The process of Claim 26, wherein the nickel-coating represents about 45% to about 60% or the total weight of the nickel-coated graphite fiber.

30. The process of Claim 21, wherein the aromatic thermoplastic liquid crystalline polymer is a polyester or a poly(ester-amide).

31. The process of Claim 30, wherein at least 50% of the bonds to ester or amide groups are to carbon atoms which are part of aromatic rings.

32. The process of Claim 31, wherein at least 75% of the bonds to ester or amide groups are to carbon atoms which are part of aromatic rings.

33. The process of Claim 26, wherein the nickel-coated graphite fiber further comprises a non-liquid-crystalline thermoplastic binder resin.

34. The process of Claim 33, wherein the binder resin comprises about 0.1% to 20% by weight of the graphite.

35. The process of Claim 34, wherein the binder resin comprises about 5% to about15% by weight of the graphite.

36. A shaped article formed according to the process of Claim 1.

37. A shaped article formed according to the process of Claim 21.

38. The shaped article of Claim 36 comprising a form of a bipolar plate.

39. The shaped article of Claim 37 comprising a form of a bipolar plate.

40. The shaped article of Claim 36 further comprising fluid distribution channels inscribed upon the surface thereof.

41. The shaped article of Claim 37 further comprising fluid distribution channels inscribed upon the surface thereof.

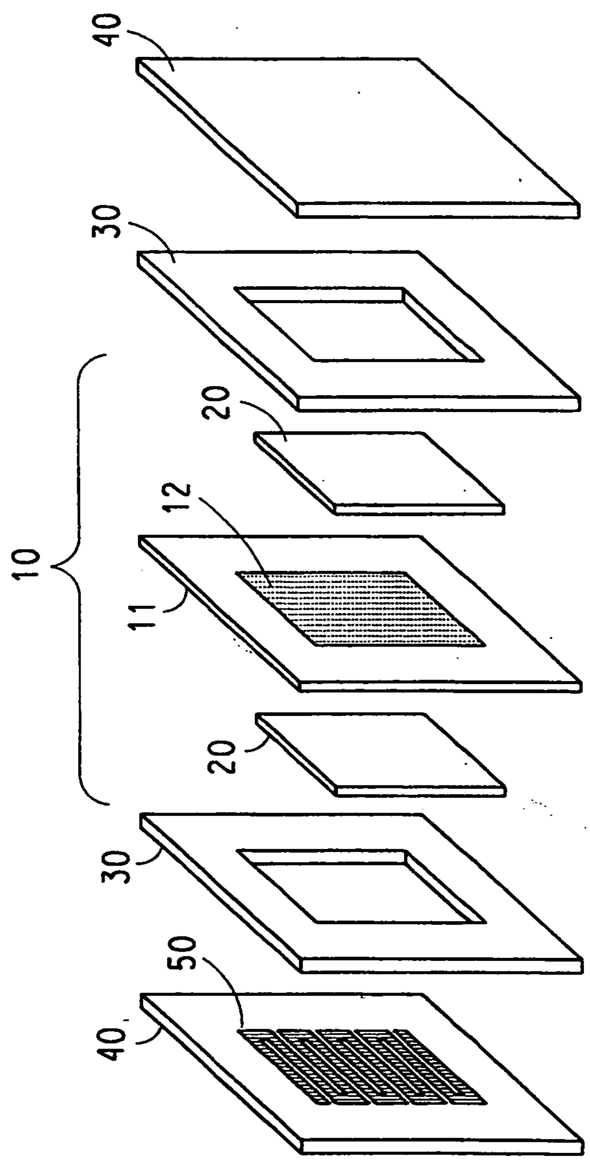

FIG. 1

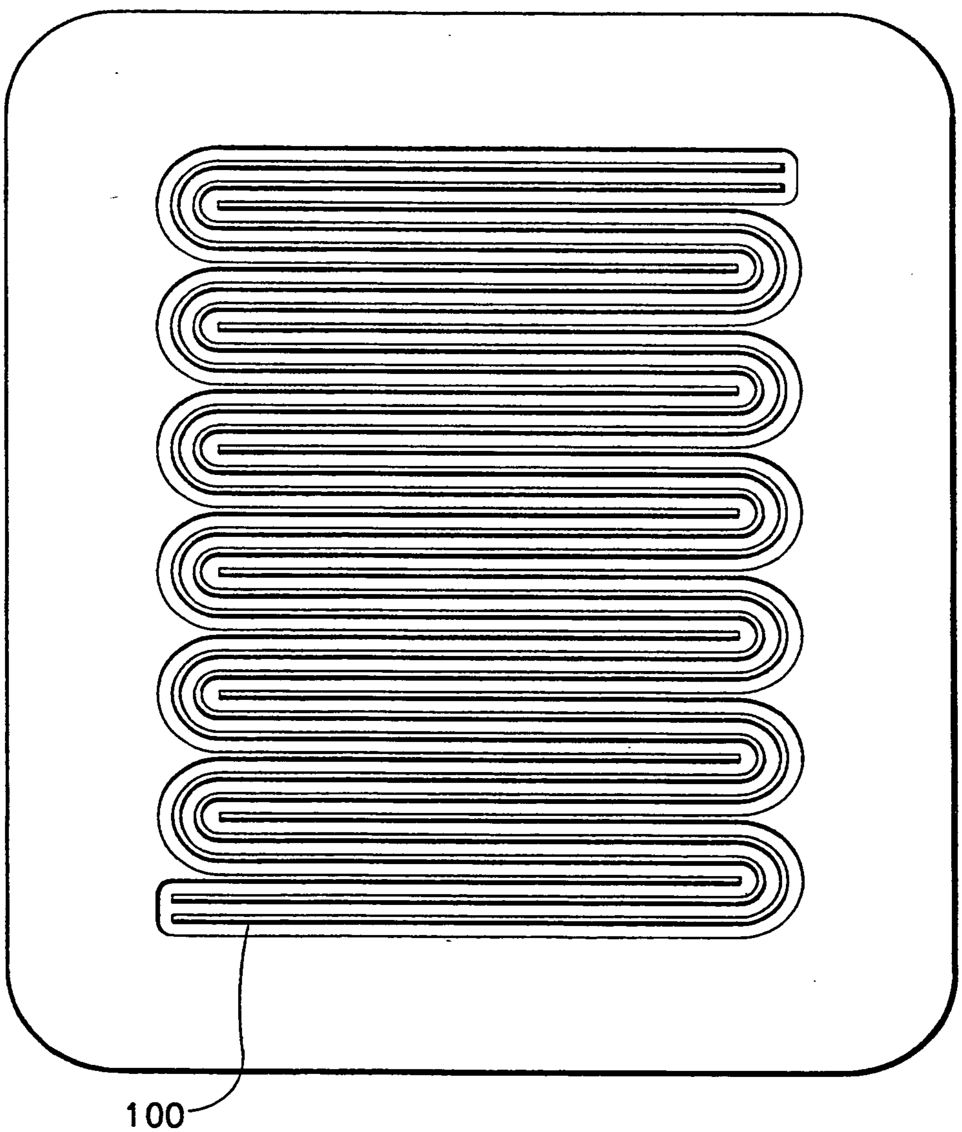

FIG. 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/01159

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01B1/20 C08K3/04 H01M8/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01B C08K H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 214 969 A (LAWRENCE RICHARD J) 29 July 1980 (1980-07-29) cited in the application the whole document	1-41
A	EP 0 485 991 A (MATRIX SCIENCE CORP) 20 May 1992 (1992-05-20) page 2, column 2, line 40 - line 43	1-41
A	EP 0 572 911 A (SUMITOMO CHEMICAL CO) 8 December 1993 (1993-12-08) the whole document	1-41
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 May 2000	31/05/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Shade, M

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INTERNATIONAL SEARCH REPORT

Inte .onal Application No
PCT/US 00/01159

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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